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REVISED HYDRAULIC FRACTURING AND NZVI INJECTION WORK PLAN OPERABLE UNIT TWO (OU-2) RÜTGERS ORGANICS CORPORATION NEASE CHEMICAL SITE, SALEM, OHIO

Prepared for:

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1.0 INTRODUCTION

This Hydraulic Fracturing Pilot-Scale Study Work Plan (Work Plan) has been prepared by Golder Associates Inc. (Golder), on behalf of RÜTGERS Organics Corporation (ROC) for Operable Unit Two (OU-2) at the Nease Chemical Site, Salem, Ohio (Site). This pilot-scale study is being performed to further evaluate the deliverability of nano-scale zero-valent iron (nZVI) based on the results of the pilot-scale study performed in November 2006 and reported in the NZVI Field Pilot Study Test Report (Golder, 2008). The 2006 activities consisted of baseline sampling, nZVI and nZVI with palladium (Pd) injection (gravity fed and pressurized injection), and six (6) rounds of sampling over a 21-week period from the start of injections. The sampling results indicated reductions in concentrations of volatile organic compounds (VOCs) and changes in groundwater geochemistry due to the effect of nZVI, including:

- Diffuse reactive zone of approximately 20-feet in radial extent (non-uniform distribution) from the injection well based on a variety of indirect indicators, including ORP, TSS, and sulfate;
- Tetrachloroethene (PCE) and Trichloroethene (TCE) were substantially degraded;
- 1,1,2,2-Tetrachloroethane (1,1,2,2-TeCA) was substantially degraded in several wells;
- *Cis*-1,2-Dichloroethene (*Cis*-1,2-DCE) was produced, likely from the breakdown of PCE and TCE and possibly 1,1,2,2-TeCA;
- Greatest reductions occurred in the injection well;
- Light hydrocarbons (ethene, ethane, methane and acetylene) indicated stronger evidence of nZVI reactions in the injection wells (NZVI-3 and NZVI-4), which may indicate that PCE reduction was incomplete in other wells during the period of the pilot test; and,
- Naturally occurring sulfate levels present a significant background demand for nZVI at the site.

Based on these results it was concluded that a second pilot-scale study is necessary to evaluate the potential for delivering nZVI more efficiently using hydraulic fracturing to enhance and further propagate the existing fracture network present in the target treatment unit (Middle Kittanning sandstone) and increase the transmissivity of this formation prior to nZVI injection. It is assumed that the current fracture network in the sandstone unit is the primary mode of contaminant transport. Therefore, the goal of this study is to re-open and further propagate fractures in this network and emplace nZVI in this system. Contaminants are then anticipated to continue to flow through this enhanced fracture network and be treated by nZVI. Golder's experience with hydraulic fracturing and nZVI injection in shallow bedrock suggests nZVI migration greater than 40-feet is possible.

2.0 ADVANCES IN NZVI REMEDY IMPLEMENTATION

Over the past several years, but particularly in the last year, significant advances have been made in understanding nZVI technology. Advances include, but are not limited to, the following key technical issues and areas of research and application:

- nZVI Mobility
- nZVI Reactivity
- Treatment Longevity
- Use of Bi-metallic Nano-Scale Particles (BNPs)
- Impact to Local Microorganisms

Following is a description of these key technical issues that have come to the forefront of nZVI technology.

2.1 nZVI Mobility

Our research and published literature indicated the need for additives to increase nZVI mobility in the subsurface (Tratnyek and Johnson, 2006, Phenerat et al., 2008, Kanel et al., 2008). Golder-supported experiments have been carried out using either soy powder or polyacrylic acid (PAA) to reduce the adsorption of nZVI on soil particles and to increase its mobility. The major conclusion from this work is the site-specificity associated with nZVI mobility. The dependence of nZVI mobility in the subsurface, and therefore radius of influence (ROI), on subsurface conditions has been established. Also, the importance of injecting nZVI using pressure-injection and including an injection additive (soy powder is recommended) has been established. In bedrock applications, the use of hydraulic fracturing has been shown to be effective in enhancing and further propagating the existing fracture networks and increasing the transmissivity of formations allowing for substantially enhanced nZVI delivery and migration.

2.2 nZVI Reactivity

Our research and published literature indicates that nZVI produced by grinding methods is less reactive than nZVI produced in the laboratory via chemical precipitation due to grinding-induced oxidation generating an iron-oxide surface coating on the produced particles. However, nZVI produced by chemical precipitation methods also has a relatively short reaction lifetime causing it to exhaust its reactivity quickly. Laboratory studies and field experiments indicated that the nZVI produced by grinding will have a similar reactivity to material made through chemical precipitation if palladium coatings are used (see Section below on use of BNP) and will maintain reactivity for a longer period. nZVI to be used in the proposed Pilot-Scale Test will be produced by grinding methods and will utilize palladium as a reactive catalyst.

2.3 nZVI Treatment Longevity

In comparison to the pilot test conducted previously at the Site, recent pilot-scale tests and full-scale treatments use much larger nZVI quantities. These experiments also show a much longer persistence of the VOC treatment with treatment lasting for greater than one (1) year from the time of injection at a large pilot-scale test site. For example, a pilot-scale test performed at a defense site in Canada resulted in continued treatment of groundwater VOCs for over 24 months. This long-term treatment has been ascribed to enhanced anaerobic bioremediation that is the result of aquifer conditioning to low oxidation-reduction potential (ORP) conditions, due to the injection of nZVI, and the addition of nutrients from the dispersant (soy powder) used during nZVI injections.

2.4 Use of Bi-metallic Nano-Scale Particles (BNPs)

The necessity of including a small amount (< 0.5% wt/wt) of palladium (Pd) on nZVI to achieve relatively rapid and efficient reactivity has been illustrated by published literature and our research. Extensive bench-scale research suggests that including Pd as a catalyst increases the reactivity of ground nZVI to a level at, or above, that of precipitated nZVI. However, it is anticipated that ground nZVI with Pd (BNP) has a longer reactive lifetime due to the ability of Pd to siphon electrons from zero-valent iron at the core of nZVI particles even with iron-oxide coatings. This chemistry is driven by the chemistry of noble metals, one of which is Pd, defined as metals that are highly resistant to oxidation. These metals become catalytically important through the concept of the galvanic series (electro-potential series). When two metals are in solution, the less noble metal (nZVI) will preferentially oxidize due to the presence of the noble metal (Pd). Electrons are siphoning from the base metal (nZVI) because the noble metal (Pd) is resistant to donating electrons. These electrons from the core of nZVI particles are brought to the particle surface and used to degrade chlorinated aliphatic hydrocarbons (CAHs).

2.5 Impact to Local Microorganisms

Microbiological testing has been performed in parallel with nZVI treatments at several sites. The methodology was designed to determine the diversity of the bacterial community represented by groundwater samples collected before and after nZVI injections. Molecular biological tools (MBTs) were used to determine the genetic make-up of samples. With strongly reducing conditions, available organic carbon and available iron (from Fe^0 oxidation), it was anticipated that a thriving biological community, capable of reductive dechlorination, would exist. In contrast, the test results suggest that after injection the diversity of microorganisms is significantly decreased. In several samples the results suggest the presence of only one (1) singular species. Results collected several months after injection suggest that microbiological diversity rebounds to pre-injection conditions with time. This understanding has led to the potential development of further bioremediation as a polishing step concurrent with microbiological diversity rebound. In particular, this impact to microbiology has been attributed to the addition of soy protein as a dispersing agent (impact is not observed using nZVI only in tests).

3.0 OVERVIEW OF HYDRAULIC FRACTURING PROCEDURES

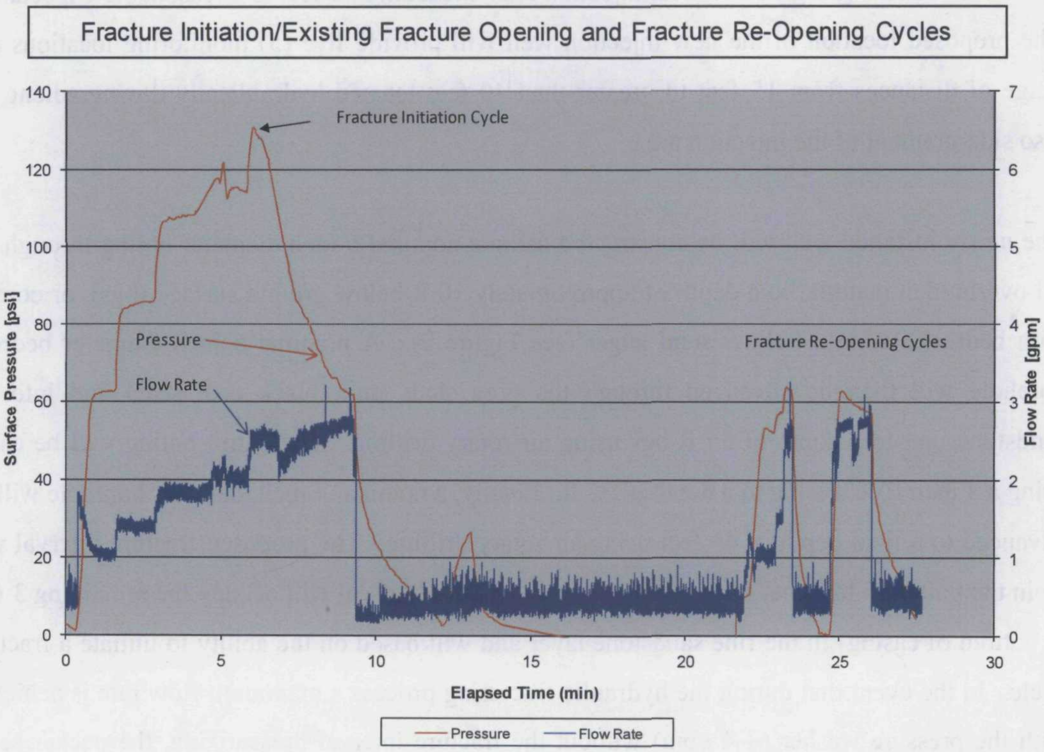
Golder has performed numerous hydraulic fracturing (hydrofracing) tests using inflatable packer systems around the globe and has previously coupled this technology with the injection of nZVI in fractured bedrock at a site in North Carolina. A pilot-study similar to that proposed herein was performed in a shallow bedrock aquifer at approximately 40 feet below ground surface (ft bgs).

The packer systems used by Golder are manufactured by Baski and are designed to provide seals up to 3,600 pound per square inch (psi) in boreholes ranging from 4-inch diameter to 8-inch diameter. To provide flow to the packer when it is deployed down-hole, water is channeled through 2-inch black steel pipe with couplings sealed using Teflon sealant. Packer inflation is achieved using 3/8-inch diameter hydraulic hose run outside the 2-inch diameter pipe.

The pumping system consists of a gas-engine, pressure washer pump with a 3,500 psi pressure maximum and a 4 gallon per minute (gpm) flow capacity. Flow is controlled through a manifold that allows for packer inflation and test zone injection from the same pumping source. The packer pressure is monitored continuously along with the pressure within the packed interval.

Testing begins by setting the packer at the desired fracture interval. Once the packer is set (it is anticipated that the packer pressure against the borehole wall will likely be approximately 500 psi) water is allowed to flow through the system with the test-zone/fracture interval pressure measurement line open, to flush air from the hydraulic hose and the 2-inch pipe. Hydraulic fracturing tests consist of one (1) pressurization cycle. The pressurization cycle begins by injecting water in the closed fracturing interval at a low flow rate (~0.5 gpm). The water injection flow rate is then slowly increased (see blue line in the Figure below). Since the fracturing interval is closed, the pressure is building up in the closed system until a maximum pressure is reached followed by a sudden drop in pressure (see the red line in the Figure below). This is the result of a fracture initiation. It is Golder's experience that under similar conditions (shallow sandstone bedrock) the fracture initiation pressure will likely be less than 300 psi. This fracture initiation pressure is likely the pressure necessary to open and propagate existing fractures (e.g., bedding plane partings) rather than the pressure to generate a primary fracture in the sandstone.

Once the water injection is stopped the newly formed fracture closes under the lithostatic pressure. A second fracturing cycle is then used to establish the fracture re-opening pressure (jacking pressure). The hydraulic jacking test consists of several constant pressure steps that are designed to define the fracture re-opening or jacking pressure. Golder anticipates this type of response and expects the re-opening pressure for this shallow bedrock system to be on the order of 50 psi to 100 psi. As indicated above, the re-opening pressure is related to the lithostatic pressure (the pressure of the rock formation above) and any pressure loss from inefficiencies. When the water injection is stopped the re-opened fracture will close under lithostatic pressure.



4.0 SCOPE OF WORK FOR HYDRAULIC FRACTURING AND SUPPLEMENTAL NZVI INJECTION PILOT-SCALE STUDY

4.1 Pilot-Scale Study Location and Injection Well Installation

The scope of work for this task is to complete *in situ* groundwater treatment using nZVI at a proposed injection well to be installed in the vicinity of existing wells NZVI-03 and PZ-6B-U. The injection well will be located approximately 12.5 feet south of well PZ-6B-U and 15 feet west of well NZVI-03 (Figure 1). Previous Golder experience with injection of nZVI following hydraulic fracturing suggests that an injection ROI exceeding 40 feet is a reasonable expectation. The proposed location of the new injection well will provide five (5) monitoring locations at a range of distances from 15 feet to greater than 40 feet located hydraulically downgradient and also side-gradient of the injection area.

The newly installed well will be constructed using a nominal 6 inch diameter boring through the till overburden material to a depth of approximately 10 ft below ground surface (bgs), or contact with bedrock, using a hollow stem auger (see Figure 2). A nominal 6 inch diameter bedrock borehole will then be advanced through the grey shale unit, black coal seam and into the sandstone unit to a depth of 35 ft bgs using air rotary drilling. The entire boring will be cased using a 4 inch PVC casing to a depth of 35 ft. Finally, a nominal 4 inch diameter borehole will be advanced to a final depth of 45 feet using air rotary drilling. The proposed fracture interval will be in the bottom 5 to 7 feet of the open borehole (the packer seal will occupy the remaining 3 feet to bottom of casing) in the fine sandstone layer and will based on the ability to initiate a fracture cycle. In the event that during the hydraulic fracturing process a maximum flow rate is achieved with the pressure washer (~ 4 gpm) without the fracture interval pressurizing, the packer setup may be lowered in the borehole to isolate a smaller fracture interval and the pressurization cycle can be reinitiated. If pressurization is not possible in the smaller interval, it will be concluded that fracturing is not necessary and injections will be performed at the backpressure achieved using a higher flow rate pump. The open borehole interval corresponds to the depth of the monitoring well screens used in the previous nZVI Pilot-Scale Study and was determined based on evaluation of the boring logs collected during the placement of these previous wells.

4.2 Hydraulic Fracturing

This injection well will be used to test the effectiveness of hydraulic fracturing to enhance and further propagate the existing fracture network present in the target treatment unit and increase the transmissivity of the formation potentially providing hydraulic connection to areas within the formation with intrinsically higher transmissivity. Following hydraulic fracturing of the borehole as described in Section 3.0, nZVI will be injected immediately under pressure in the newly installed well. Prior to hydraulically fracturing the newly installed well a baseline groundwater sampling event will be performed along with a slug test to evaluate the hydraulic conductivity of the formation prior to the pilot-scale test. In addition, a second slug test will be performed after hydraulic fracturing and injection of nZVI to evaluate the hydraulic conductivity of the formation.

4.3 nZVI Injections

nZVI injections will be performed immediately following hydraulic fracturing and testing of the proposed injection well. nZVI, freshly manufactured using the grinding method (less than one week prior to injection) will be used for this study. Palladium (in the form of palladium acetate) will be added to nZVI at the site to maximize the nZVI reactivity and treatment longevity. The total dose of nZVI with palladium coating will be approximately 75 kilograms (kg) and will be injected over a period of 3 to 5 days.

nZVI will be injected as a slurry prepared on-Site using potable water. The iron slurry will be prepared in a holding tank and the slurry will be transferred from the holding tank to the injection well by pressurized injection. Downgradient wells NZVI-01, NZVI-02, NZVI-03 and nZVI-04 along with side-gradient well PZ-6B-U will be used as monitoring points for Pilot-Scale Study evaluation of ROI. As secondary objectives of the study, treatment effectiveness and treatment longevity will also be evaluated through progress monitoring (see Section 4.4).

nZVI will be produced by Golder and transported to the Site in two (2), 50 kg drums containing 800 grams per liter (g/L) nZVI in water. nZVI will be injected as a diluted slurry suspension made on-Site with potable water. Initially, nZVI material will be mixed in the production barrel using a hand-held blade-type power mixer. After the nZVI is re-suspended in the slurry, palladium will then be added to the mixing tank at approximately 0.05 percent of the nZVI weight (0.05% wt/wt). The dense slurry will then be transferred to a 300 gallon poly mixing tank where potable water will be added to achieve the desired slurry density. Golder anticipates that a slurry density of a minimum of 10 g/L will be used and modified based on injection pressure and flow rate monitoring. Soy protein powder (SoyLink Gold 300 Soybean Flour) will then be added to the mixing tank at approximately 20 percent of the nZVI weight (20% wt/wt). The mixing tank will be stirred continuously using an in-tank mixing system. The slurry will be transferred from the mixing tank to the well-head using a 4-inch diameter Grundfos pump. The injection header system includes a flow meter and a standard back-pressure gauge. Golder anticipates injecting at a rate of approximately six (6) gpm with a goal of maintain a back-pressure in the nZVI injection line consistent with the observed fracture re-opening pressure.

4.4 Groundwater Monitoring

The percent reduction in VOCs will be monitored at the proposed injection well and also downgradient wells NZVI-01, NZVI-02, NZVI-03 and nZVI-04 along with side-gradient well PZ-6B-U (six total sampling locations). One (1) baseline and two (2) rounds of post injection groundwater samples (total of three sampling rounds[1]) will be collected for a period of a minimum of three (3) months. The post-injection sampling will be conducted one (1) month and three (3) months after nZVI injection, respectively.

Groundwater samples will be analyzed for TCL volatile organics (including chlorobenzene and dichlorobenzenes), natural attenuation parameters (NAPs) including: total organic carbon (TOC), nitrate, sulfate, sulfide, methane, ethane, ethene and total iron, and standard field parameters [Turbidity, Oxidation Reduction Potential (ORP), Dissolved Oxygen (DO), pH, Specific Conductivity and Temperature]. All groundwater samples will be collected using dedicated Teflon-lined tubing. All the proposed site work will be conducted in accordance with the approved Sampling and Analysis Plan.

Three days of datalogger monitoring will be conducted during nZVI injection. Oxidation reduction potential (ORP), dissolved oxygen (DO) and pH will be monitored in two downgradient monitoring wells (NZVI-2 and NZVI-3) using electronic data loggers to evaluate the continuous changes of these parameters as the reactive front advances in the subsurface.

[1] Only three (3) rounds of groundwater monitoring are proposed since the main objective of this test is to identify the ROI of nZVI treatment and not the actual treatment efficiency.

4.5 Reporting

A letter report will be prepared summarizing the results of the Pilot-Scale Study. This report will include the following:

- Report summarizing implementation, results and a summary of the design basis for the full-scale nZVI remedy;
- Tables and graphs summarizing the groundwater monitoring results;
- Injection well borehole log; and,
- Figures showing groundwater concentrations.

4.6 References

Tratnyek, P.G. and Johnson, R.L. Nanotechnologies for Environmental Cleanup. *Nanotoday*. **2006**. Vol. 1. No. 2, 44-48. 2.

Phenrat, T., Saleh, N., Sirk, K., Kim, H., Matyjaszewski, K., Titlton, R., Lowry, G.V. Stabilization of Aqueous Nanoscale Zerovalent Iron Dispersions by Anionic Polyelectrolytes: Adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation. *J Nanoparticle Res*. **2008**. *10*. 795-814. 3.

Kanel, S.R., Goswami, R.R., Clement, T.P., Barnett, M.O. and Zhao, D. Two Dimensional Transport Characteristics of Surface Stabilized Zero-valent Iron Nanoparticles in Porous Media. *Environ. Sci. Technol*. **2008**. *42*, 896-900.

4.7 Closing

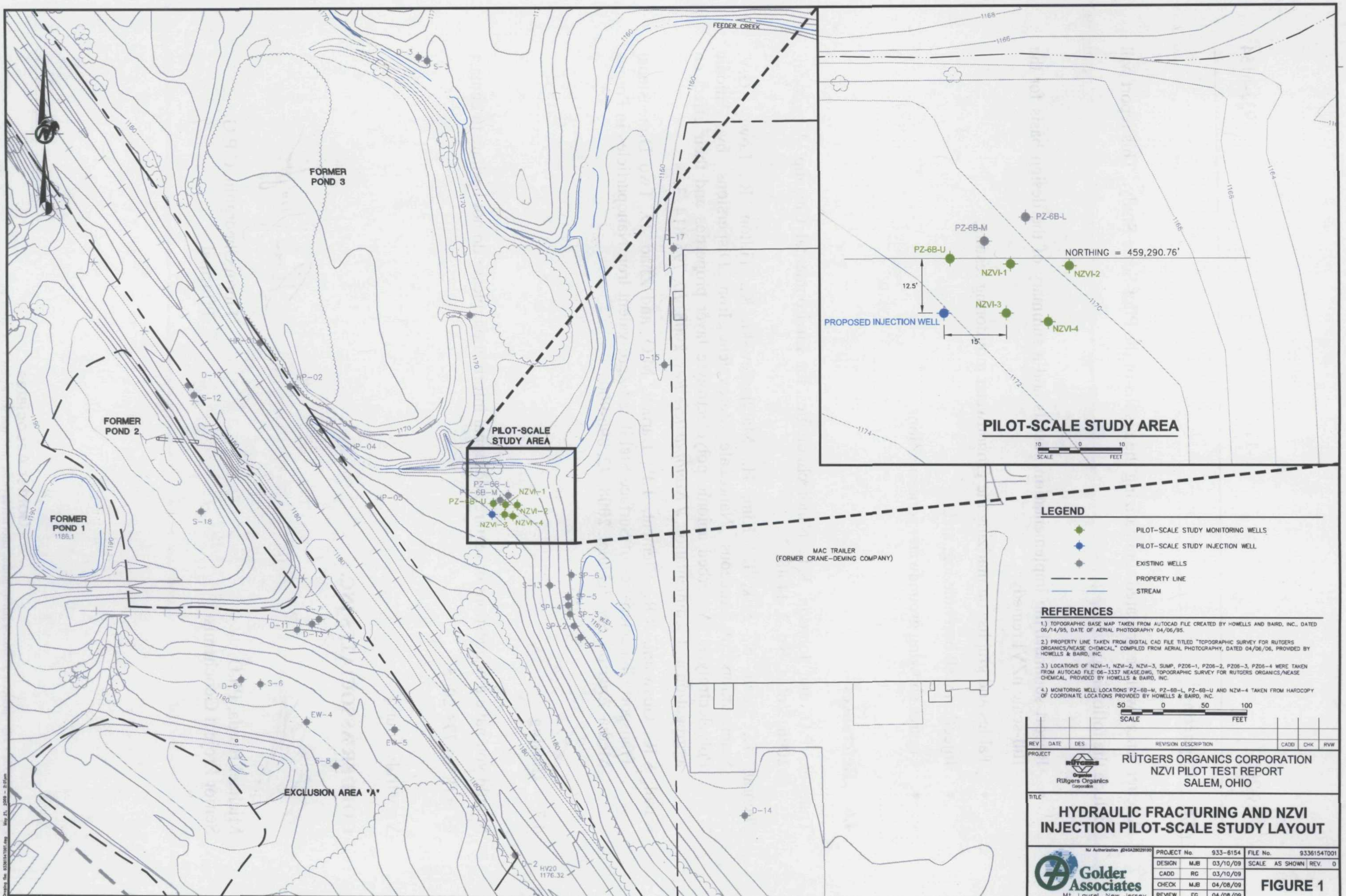
Should you have any questions or require additional information, please do not hesitate to contact us at (856) 793-2005.

Very truly yours,

GOLDER ASSOCIATES INC.

Michael Borda, Ph.D.
Senior Project Geochemist

Florin Gheorghiu, C.P.G.
Principal



LEGEND

PILOT-SCALE STUDY MONITORING WELLS
PILOT-SCALE STUDY INJECTION WELL
EXISTING WELLS
PROPERTY LINE
STREAM

REFERENCES

1.) TOPOGRAPHIC BASE MAP TAKEN FROM AUTOCAD FILE CREATED BY HOWELLS AND BAIRD, INC., DATED 06/14/95, DATE OF AERIAL PHOTOGRAPHY 04/06/95.

2.) PROPERTY LINE TAKEN FROM DIGITAL CAD FILE TITLED "TOPOGRAPHIC SURVEY FOR RUTGERS ORGANICS/NEASE CHEMICAL," COMPILED FROM AERIAL PHOTOGRAPHY, DATED 04/06/06, PROVIDED BY HOWELLS & BAIRD, INC.

3.) LOCATIONS OF NZVI-1, NZVI-2, NZVI-3, SUMP, PZ06-1, PZ06-2, PZ06-3, PZ06-4 WERE TAKEN FROM AUTOCAD FILE 06-3337 NEASE.DWG, TOPOGRAPHIC SURVEY FOR RUTGERS ORGANICS/NEASE CHEMICAL, PROVIDED BY HOWELLS & BAIRD, INC.

4.) MONITORING WELL LOCATIONS PZ-6B-M, PZ-6B-L, PZ-6B-U AND NZVI-4 TAKEN FROM HARDCOPY OF COORDINATE LOCATIONS PROVIDED BY HOWELLS & BAIRD, INC.

REV	DATE	DES	REVISION DESCRIPTION	CADD	CHK	RVW

PROJECT

RÜTGERS ORGANICS CORPORATION
NZVI PILOT TEST REPORT
SALEM, OHIO

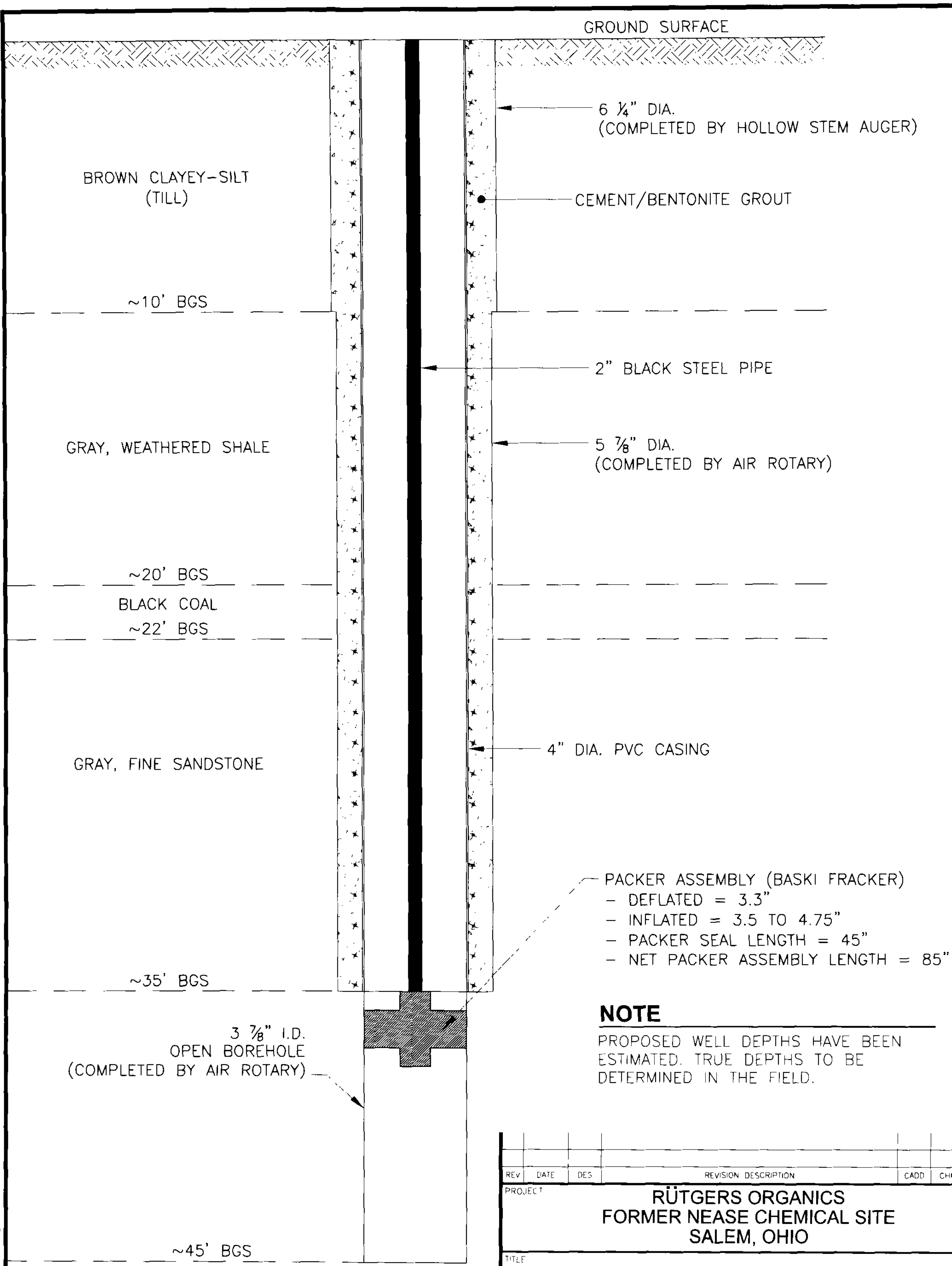
TITLE

HYDRAULIC FRACTURING AND NZVI INJECTION PILOT-SCALE STUDY LAYOUT

Golder Associates
Mt. Laurel, New Jersey

PROJECT No.		933-6154	FILE No. 9336154T001
DESIGN	MJB	03/10/09	SCALE AS SHOWN REV. 0
CADD	RG	03/10/09	
CHECK	MJB	04/08/09	
REVIEW	FG	04/08/09	

FIGURE 1



NOTE

PROPOSED WELL DEPTHS HAVE BEEN ESTIMATED. TRUE DEPTHS TO BE DETERMINED IN THE FIELD.

SCALE: VERTICAL = 1" = 5'
HORIZONTAL = EXAGGERATED, NTS

REV	DATE	DES	REVISION DESCRIPTION	CADD	CHK	RVW

PROJECT
RÜTGERS ORGANICS
FORMER NEASE CHEMICAL SITE
SALEM, OHIO

TITLE
NZVI INJECTION WELL DESIGN

NJ Authorization #24GA28029100

Golder Associates
Mt. Laurel, New Jersey

PROJECT No.		933-6154	FILE No. 9336154N002
DESIGN	CJL	05/19/09	SCALE AS SHOWN REV 0
CADD	GLS	05/21/09	
CHECK	MJB	05/21/09	**FIGURE 2**
REVIEW	PSF	05/21/09	

Drawing file 9336154N002.dwg May 21, 2009 - 2:05pm